THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME NITRO COMPOUNDS

BY

MARVIN DEN HERDER, JR.

A.B., Hope College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

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Acknowledgment

The author wishes to express his appreciation to Professor W. H. Rodebush for his supervision of this investigation.

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The ultraviolet absorption spectra of some nitroparaffins, namely: nitromethane, nitroethane and nitroisopropane were observed to determine their specific absorption and to investigate the nitro to aci shift which is observed in basic solutions. These compounds were investigated in solution. The solvents used were *n*-hexane, aqueius HCl, sodium hydroxide solutions and boric acid buffered solutions of various *p*H's.

The instrument used in this study of these compounds was a Bausch and Lomb Medium Quartz Spectrograph equipped with a sector photometer. The spectra were permanently recorded on Eastman polychrome photographic plates. The light source was a spark formed between two tungsten steel electrodes. The light beam was split into two beams of equal intensities by a system of quartz rhombs. The upper half of the split beam passed through the solvent and the lower half passed through the solution. The split beam was brought into juxtaposition by quartz rhombs and then passed into the spectograph which records the spectrum on the photographic plates. Numerous exposures were made of each sample at different extinction values. The extinction values were controlled by varying the openings in the sector wheel. From the match points on our plates we determined the wave lengths which correspond to the extinction values. The absorption curves were obtained by plotting the molecular extinction coefficient as ordinate against the wave length in Angstrom units, A., as abscissa. The molecular extinction coefficient was obtained by use of the well known Beer's Law.

$$I = I_o 10^{-Ecd}$$

The conclusions obtained from the curves were deduced from the position and intensity of the absorption bands and the change

in absorption caused by the formation of the aci compounds when the nitro compounds are in basic solutions.

The typical absorption of the nitro group was found to be a weak band occurring at a wave length of about 2730 A. This absorption is caused by the electronic shift between the two oxygen atoms. The maximum absorption of this band was found to be at $\lambda = 2700$ A. and $E = 14.0$ for nitromethane. $\lambda = 2720$ A. and $E = 17.7$ for nitroethane and $\lambda = 2730$ A. and $E = 21.4$ for nitroisopropane. These values are given for the absorption observed in 0.1 M HCl solutions.

The aci forms of these compounds were found by determining the absorption in 0.1 M NaOH. There is practically no absorption above 2720 A. The absorption peaks for all three compounds occur at wave lengths below the limit of the instrument used. The E values are well above 1000 and occur below 2300 A. Difficulty is encountered with nitromethane in basic solutions as nitromethane tends to dimerize and form the sodium salt of methazonic acid. This gives an intense absorption and prohibits the examination of the absorption of the true aci form.

An excess of nitro compound was added to sodium hydroxide solutions. After the solutions were allowed to come to equilibrium the absorption curves were determined. Under these conditions the absorption of equilibrium mixtures of nitro and aci compounds are measured. No matter what the ratio of aci to nitro, the curves passed through a common point called the isobestic point. This point for nitroethane is at $E = 17.6$ and $\lambda = 2690$ A. The point for nitroisopropane is at $E = 20.7$ and $\lambda = 2685$ A. These same isobestic points were observed when the velosity of the reaction was followed in borate buffers. This nitro to aci reaction is slow as in buffered solutions of *p*H's between 9 and 10 the reaction did not seem to reach equilibrium even after 48 hours.

The equilibrium constant, K_a, was defined as

$$K_a = \frac{(H^+)\ (Aci^-)}{(Nitro)}$$

The ration of Aci$^-$ to nitro was found from the distances between

the observed equilibrium curves and the 100% Aci— curve and the 100% Nitro curve. The equation used is

$$\frac{(\text{Aci}^-)}{(\text{Nitro})} = \frac{E_a - E_c}{E_c - E_b}$$

E_a, E_b, and E_c are the molecular extinction coefficients for 100% Nitro, 100% Aci— and equilibrium solutions respectively. The hydrogen ion concentration was determined by a Beckman, Model F, *p*H meter.

The average K_a for nitroethane is 3.53×10^{-9}. The K_a for nitroisopropane is 2.11×10^{-8}. The K_a's obtained in the buffered solutions were lower and erratic. This is probably due to non-equilibrium conditions.

The results obtained show that the aci to nitro shift is a reaction which occurs by the direct formation of a negative charge on one of the oxygen atoms and doesn't involve the occurrence of a form which has the negative charge on the carbon atom. This form is not even present as an intermediate.

These observations question the use of the aci form, which involves the charge on the carbon atom, in the explanation sometimes given for the retention, in alcohol plus sodium alcoholate solutions, of optical activity of optically active nitro compounds.

Vita

The writer was born September 27, 1919 in Grand Haven, Michigan. He received his elementary and high school education in Grand Haven and was graduated from high school in June, 1937. He attended Hope College at Holland, Michigan from 1937 to 1941 and received the A.B. degree in June, 1941. During the year 1941-42 he held a Rockefeller Foundation Research Fellowship at the University of Illinois. He held an assistantship in physical chemistry for the year 1942-43 and a University of Illinois Fellowship for the year 1943-44. He is a member of Phi Lambda Upsilon and an associate member of Sigma Xi.

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